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(21) International Application Number: PCT/DK90/00082 (22) International Filing Date: 30 March 1990 (30.03.90) (30) Priority data: 1589/89 31 March 1989 (31.03.89) DK (71) Applicant (for all designated States except US): NOVO-NORDISK A/S [DK/DK]; Novo Allé, DK-2880 Bagsvaerd (DK). (72) Inventors; and (75) Inventors/Applicants (for US only) : SOERENSEN, Niels, Henrik [DK/DK]; Dyrelunden 1, DK-3320 Skaevinge (DK). FRENDRUP, Willy [DK/DK]; Indelukket 37, DK-2900 Hellerup (DK). RYDIN, Stefan [DK/DK]; Hoeje Taastrup Boulevard 49, DK-2630 Taastrup (DK).	(74) Common Representative: NOVO-NORDISK A/S; Patent Dept., Novo Allé, DK-2880 Bagsvaerd (DK). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published With international search report.	
(54) Title: ENZYMATIC METHOD FOR UNHAIRING OF HIDES OR SKINS (57) Abstract The enzymatic method for unhairing of hides or skins comprises treating the hides or skins with an aqueous float with a pH value of 3.5 to 5.0 and containing an organic acid and a special carbohydrase preparation which is able to pass a specified standard test for unhairing carbohydrase activity. The method is efficient and cheap and provides a good compromise en regard to treatment time, maintenance of grain and pollution.		

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ENZYMATIC METHOD FOR UNHAIRING OF HIDES OR SKINS

Enzymatic methods for unhairing of hides or skins for leather manufacture is a well-defined technology which is described in detail in the patent literature and elsewhere.

5 The methods for unhairing of hides or skins can be categorized in two main groups, i.e. the hair dissolving methods, which are all chemical type unhairing methods, and the hair preserving methods, some of which are of the chemical type and some others are of the enzymatic type. The
10 hair preserving unhairing methods exhibit the following advantages vis-a-vis the hair dissolving methods: they generate less pollution in as much as the waste water exhibits a lower BOD (Biological Oxygen Demand) and nitrogen content, due to the saving of the hair, and a lower sulfide
15 concentration and they often generate a larger area yield. The method according to the invention is a hair preserving unhairing method.

Those prior art preserving unhairing methods which are most related to the method according to the invention are
20 the following.

The enzymatic unhairing process described in US 3,840,433 is performed with alkaline resistant proteolytic enzymes at high pH values. The process is relatively fast, i.e. around 24 hours, but a disadvantage is the tendency to
25 grain damage. Also, the high pH value is a disadvantage, due to the strong alkaline swelling of the hide.

The enzymatic unhairing process described in European patent application with publication No. 0 180 135 is performed in an aqueous float with a culture of lactic acid
30 bacteria whereby both metabolically generated enzymes and organic acids, predominantly lactic acid, are present in the aqueous float. This unhairing process is efficient but the reaction time is long, i.e. 3 days or more.

The Erhavit process described in J. Christner, The
35 pros and cons of a hair save process in the beamhouse, JALCA 83, 183-92 (1988), and T. Taeger, Technologieänderungen in

den Nasswerkstätten der Lederherstellung in den nächsten zehn Jahren (lecture, Nordisk Læder Kemiker Forenings kongres, Tyløsand 1988-08-20) is quite efficient and can be performed rapidly, i.e. in 24 hours or less, but the waste water is 5 heavily polluted with sulfite and the treatment of the waste water in order to meet the minimum environmental requirements fixed by the authorities is expensive.

The enzymatic hair preserving unhairing method described in DE published application No. 3513253 is 10 relatively fast and it does not damage the grain and does not give rise to any major pollution problems. However, due to the necessary pressure which has to be generated, the method requires an expensive equipment. The method is not used in any production plant and it is doubtful whether it will ever 15 be used in a production plant.

Thus, there is a need for a method for efficient and cheap enzymatic unhairing of hides or skins, which provides a good compromise in regard to treatment time, maintenance of grain and pollution.

20 According to the invention it has been found that certain carbohydrases, which are able to pass the below indicated standard test as a dehairing carbohydrase fulfills this need under defined unhairing conditions.

This standard test is a laboratory scale method for 25 evaluation of unhairing of hides.

Salted sections of hides are soaked in water as follows:

300% water, 20°C, 2 hours (dirt soak)

Drainage

30 300% water, 20°C, overnight (main soak)

all percentages being based on the weight of hides or hide pieces.

Circular hide pieces (diameter: 4.5 cm) are punched from three different positions on the hide sections, namely 35 bend, belly and shoulder. 3 pieces (average total weight 30

g) are contained in one 300 ml Erlenmeyer flask. The trials are carried out in a thermostatted shaker bath.

The hides are treated according to the following standard recipe:

- 5 300% water
 2.4% NaCl
 Shaken 5 minutes at 32°C
 addition of: 0.15% sorbic acid (stabilizer)
 2.00% of carbohydrase preparation
10 2.00% of lactic acid
 shaken at 32°C and pH 3.9 - 4.0

The hair looseness is evaluated after 23 hours, 30 hours, 48 hours, and 72 hours according to a relative scale from 0 to 4. Independently of each other two experienced 15 leather scientists quantified the unhairing effect of the leather pieces.

To obtain reproducible results two standard samples were enclosed in every experiment (2% lactic acid without any enzyme and 2% lactic acid with enzyme). The following notes 20 in a scale from 0 to 4 was used:

- 4 = all hair removed
3 = more than 75% of the hair could be scraped off by a finger nail.
2 = more than 75% of the hair could be pulled off without the 25 use of any strength.
1 = more than 75% of the hair could be pulled off by using some strength.
0 = no hair loosening effect could be observed.

If after 30 hours of treatment in relation to the 30 above standard test a note of at least 2 is obtained or if after 48 hours of treatment in relation to the above standard test a note of at least 2 - 3 is obtained the carbohydrase is a carbohydrase inside the scope of the invention.

The enzymatic method for unhairing of hides or skins according to the invention comprises treating the hides or skins with an aqueous float with a pH-value of 3.5 to 5.0, preferably 3.8 to 4.2, and containing an organic acid, and a
5 carbohydrase preparation which is able to pass the above indicated standard test as an unhairing carbohydrase.

Surprisingly, it has been found that the method according to the invention can be carried to completion in less than 24 hours, that the method according to the
10 invention does not give rise to any grain damage when used in a proper dosage, that the waste water originating from the method according to the invention only represents minimal pollution problems, especially in regard to nitrogen, and that it can be carried out with existing conventional
15 equipment in an economically sound manner.

It is to be understood that high dosages of carbohydrase preparations within the scope of the invention are to be used in combination with low unhairing times, and vice versa.

20 DE 1 230 169 describes an unhairing method by means of carbohydrases. However, the known unhairing with carbohydrases has to be carried out together with proteases and at higher pH-values than the unhairing method according to the invention.

25 In a preferred embodiment of the method according to the invention the organic acid is formic and/or acetic acid and/or oxalic acid and/or lactic acid. These acids are cheap, and they are fully satisfactory in relation to the invention.

30 In a preferred embodiment of the method according to the invention the unhairing float contains the carbohydrase preparation in an amount sufficient for obtaining satisfactory unhairing in less than 24 hours, the salt concentration of the unhairing float is between 0.5% and
35 1.5%, and the weight proportion between the wet hides or skins and the unhairing float is between 1:0.5 and 1:4. In this manner acid swelling is avoided.

In a preferred embodiment of the method according to the invention the carbohydrase preparation is an SPS-ase preparation. Such preparation is described in GB 2,115,820. A most satisfactory unhairing is obtained in this embodiment.

5 As the SPS-ase preparation was developed in order to break down vegetable carbohydrates, it is surprising that this carbohydrase is able also to break down animal carbohydrates.

Reference is made to the following examples, which illustrate the method according to the invention, both on a laboratory scale, on a pilot plant scale, and on a semi-production scale.

10

EXAMPLES

EXAMPLE 1

Salted hides were soaked and fleshed. After this treatment they were divided into halves which were cut into ten pieces (25 · 50 cm) and numbered according to their position on the hide. Twenty pieces from each position were obtained. The pieces from the same position were mixed and for each experiment one piece from each position was used in order to obtain an average hide. Subsequently, the pieces were salted and stored at 4°C for at least 4 weeks.

15

20

The experiments were carried out according to a standardized tanning process normally used at the Leather Research Center, Technological Institute in Denmark. The unhairing of the hides was, however, changed as specified in Table 1. Two different unhairing systems were used in these experiments.

25

Table 1

UNHAIRING PROCESS OF THE HIDE PIECES IN THE EXAMPLE

<u>Unhairing System 1</u>		<u>Unhairing System 2</u>
300% water	32°C	300% water
5 2.40% NaCl	5 min	2.40% NaCl
2.00% lactic acid (90%)	32°C	2.00% lactic acid (90%)
0.15% sorbic acid		0.15% sorbic acid
		0.30% SP 423 (SPS-ase)

The above percentages are as a weight basis and 10 related to the weight of the hide.

As appears from Table 1, the difference between the two unhairing systems was the addition of 0.3% SP 423 in unhairing system 2. The SP 423 SPS-ase preparation exhibited an SPS-ase activity of around 35 SPS-ase units/g of SP 423 15 preparation.

The time for unhairing was 3 days in unhairing system 1 while the unhairing time was approximately 1 day in unhairing system 2 where the SPS-ase preparation was added.

EXAMPLE 2

20 In order to evaluate the effect of different enzymes on the unhairing, when added together with lactic acid at a low pH of 3.8-4.0, experiments were carried out in 500 ml Erlenmeyer Flasks. The flasks were introduced into a thermostatically controlled water bath at 32°C and shaken for 25 48 hours.

Every flask contained three different small circular pieces of hide (diameter 4.5 cm). The pieces were cut from three different positions on the hide, namely bend, belly and shoulder. The average weight of the three hide 30 pieces was 30 g and the medium used in the example is given in Table 2.

Table 2

MEDIUM FOR UNHAIRING IN EXAMPLE 2 (W/W BASED ON THE HIDE WEIGHT)

300% water
 5 2.40% NaCl
 0.15% sorbic acid (stabilizer)
 2.20% lactic acid
 2.00% of enzyme

The pH was 3.8 - 4.0 during the experiments and the temperature 32°C. The effect of the enzyme on the unhairing was estimated visually after 6 h, 24 h, 30 h and 48 h. The enzymes were then divided into groups according to their effect. The results are shown in Table 3.

Table 3

15 UNHAIRING EFFECT OF DIFFERENT ENZYMES

	<u>6 h</u>	<u>24 h</u>	<u>30 h</u>	<u>48 h</u>	
Papain	0	2	3	3	large effect
SP 423 (SPS-ase product)	0	1	2	3	
20 Gamanase	0	1	2	2-3	
Pectinex	0	1	2	2-3	
Pectinex AR	0	1	1-2	2-3	
Glucanex	0	1	1-2	2	small effect
Cereflo	0	1	1	2	
25 Finizym	0	1	1	2	
Neutrase	0	1	1-2	2	
Ceremix	0	1	1-2	2	
Novozym 188	0	1	2	2	
Rennilase	0	0	1	2	no effect
30 Celluclast	0	0	1	2	
Lysozyme	0	0	1	2	

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Celluzyyme	0	0	1	2
Lactozyyme	0	0	1	2
Lactic acid but no enzyme	0	0	1	2
5 No enzyme and no lactic acid (only water)	0	0	0	0

As appears from Table 3, papain produces a large unhairing effect. However, papain is not a carbohydrase and thus is outside the scope of the invention. Furthermore it generates grain damage and thus does not fulfil the purpose of the invention. Some of the enzymes listed in Table 3 with lower effect than SPS-ase are inexpensive but their effect is too low for commercial exploitation. Thus, Table 3 demonstrates the inventive concept which is the use of a specified carbohydrase preparation for unhairing.

EXAMPLE 3

The combined effect from the organic acid and the enzyme was investigated as follows:

- 20 Recipe I standard recipe, but no enzyme
 Recipe II standard recipe; carbohydrase: SP 423
 Recipe III standard recipe without lactic acid;
 carbohydrase: SP 423, and pH adjusted with HCl

Results

25

	Hair loosening effect			
	23	30	48	72
30 Recipe I	0	0	2	2
II	1	1	3	3
III	0	0	1	3

Conclusion

Organic acid together with the SP 423 enzyme gives the best hair loosening effect, whereas organic acid alone or enzyme alone do not provide the same positive results.

5 **EXAMPLE 4**

To compare the effect from formic acid with lactic acid the following trial was conducted:

Recipe IV standard recipe; carbohydase: SP 423
Recipe V standard recipe except 1% formic acid instead
10 of 2% lactic acid; carbohydase: SP 423

Results

	Hair loosening effect			
	23	30	48	72
15 Recipe IV	1	1	3	3
V	1	1	3	3

It appears that formic acid as well as lactic acid
20 can be used in the unhairing recipe.

EXAMPLE 5

A recipe for a pilot plant trial comprising the enzymatic unhairing process.

Raw material

25 Already fleshed salted hide sections from Danish
red cows, average weight 800 g, selected from different

regions of whole cow hides. 10 such sections are contained in each drum (Dosemat small scale steel drum).

Recipe:

Dirt soak

5 300% water

Drum running 1 hour at 20°C

Drain float

Main soak

300% water

10 0.01% Neutrase 1.5 MG (Novo protease)

pH adjusted with 20% formic acid to 5.5

Drum running 4 hours at 28°C

Drain float

Unhairing

15 75% water

0.8% NaCl

Running 15 minutes at 32°C

then adding:

0.3% SP 423

20 0.25% Baymol 34107 (tenside)

pH is maintained at pH 3.8 by means of automatical titration with 20% formic acid.

Running 19 hours at 32°C

Drain float through filter

25 Dehairing note at this stage: 3

The function of the following three steps was the removal of the still remaining small amounts of residual hair after a mechanical hair removal.

Rinsing

150% water

Running 10 minutes at 20°C

Drain float through filter

5 After liming

2% Na_2S (60%) in 10% water

Running 30 minutes at 20°C

No drainage

100% water

10 3% $\text{Ca}(\text{OH})_2$

Running 1 hour 30 minutes at 20°C

Drain float

Rinsing

150% water

15 Running 15 minutes at 20°C

Drain float

Dehairing note at this stage: 4

EXAMPLE 6

In order to evaluate the process at pilot scale it was performed at a tannery producing high quality upholstery leather. The process was performed in a Dosemat drum and 30 salted bovine hides were used as raw material (salt weight 849 kg). The following recipe was used:

Dirt soak

25 100% water at 20°C for 1 hour

Drain

Main soak

100% water at 28°C for 4 hours

0.9% Fereon M301 protease, soaking enzyme.

Formic acid to pH 4.5 (2.4% was used)

5 Drain

Unhairing

75% water at 32°C for 15 minutes

0.8% salt

No drain

10 0.3% SP 423 at 32°C for 19 hours

0.25% Baymol 34107

pH-control using formic acid (1:5) to pH 3.8

Drain

Washing

15 100% water at 20°C for 30 minutes

Drain

Dehairing note at this stage: 3-4

Liming

2% Na₂S (60%) at 20°C for 30 minutes

20 10% water

No drain

100% water at 20°C for 1 1/2 hour

3% Ca(OH)₂

Drain

25 Washing

100% water at 20°C for 15 minutes

Drain

Dehairing note at this stage: 4

After the last washing the hides were processed according to the standard recipe of the tannery. At several occasions during the unhairing step the free hair in the drum was filtered away from the float by recirculation of the 5 float through a rotating filter aid. The recovered hair showed an intact structure.

The produced crust leather was examined visually by the tannery's technical staff and after passing the test it was sold to customers as high quality leather.

CLAIMS

1. Enzymatic method for unhairing of hides or skins, which comprises treating the hides or skins with an aqueous float with a pH value of 3.5 to 5, preferably 3.8 to 4.2, and
5 containing an organic acid and a carbohydrase preparation which is able to pass the standard test in the specification as an unhairing carbohydrase.
2. Method according to Claim 1, wherein the organic acid is formic and/or acetic acid and/or oxalic acid and/or
10 lactic acid.
3. Method according to Claims 1 or 2, wherein the unhairing float contains the carbohydrase preparation in an amount sufficient for obtaining satisfactory unhairing in less than 24 hours, wherein the salt concentration of the
15 unhairing float is between 0.5% and 1.5%, and wherein the weight proportion between the wet hides or skins and the unhairing float is between 1:0.5 and 1:4.
4. Method according to Claims 1 - 3, wherein the carbohydrase preparation is an SPS-ase preparation.

INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 90/00082

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 14 C 1/06																				
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="height: 40px; vertical-align: bottom;">C 14 C</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div> <p>SE,DK,FI,NO classes as above</p>			Classification System	Classification Symbols	IPC5	C 14 C														
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IPC5	C 14 C																			
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>GB, A, 2115820 (NOVO INDUSTRI A/S) 14 September 1983, see page 1, line 13 - line 20 --</td> <td style="text-align: center; vertical-align: top;">1,4</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>Derwent's abstract, No. 87- 6 262/01, SU 1 234 430, publ. week 8701 --</td> <td style="text-align: center; vertical-align: top;">1-3</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A2, 0180135 (RÖHM GMBH) 7 May 1986, see claim 1 --</td> <td style="text-align: center; vertical-align: top;">1-3</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 3203868 (O.G.DARMSTADT) 31 August 1965, see claim 1 --</td> <td style="text-align: center; vertical-align: top;">1-3</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>FR, E, 67571 (RÖHM & HAAS G.M.B.H.) 14 March 1958, see claim 1 -----</td> <td style="text-align: center; vertical-align: top;">1,4</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	GB, A, 2115820 (NOVO INDUSTRI A/S) 14 September 1983, see page 1, line 13 - line 20 --	1,4	A	Derwent's abstract, No. 87- 6 262/01, SU 1 234 430, publ. week 8701 --	1-3	A	EP, A2, 0180135 (RÖHM GMBH) 7 May 1986, see claim 1 --	1-3	A	US, A, 3203868 (O.G.DARMSTADT) 31 August 1965, see claim 1 --	1-3	A	FR, E, 67571 (RÖHM & HAAS G.M.B.H.) 14 March 1958, see claim 1 -----	1,4
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																				
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">19th June 1990</td> <td style="height: 40px; vertical-align: bottom;">1990 -07- 03</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom; text-align: center;">SWEDISH PATENT OFFICE</td> <td style="height: 40px; vertical-align: bottom; text-align: center;">Inga-Karin Petersson</td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	19th June 1990	1990 -07- 03	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	Inga-Karin Petersson										
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 90/00082**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on **90-05-24**
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		AU-B- 556762	86-11-20
		AU-D- 9172082	83-06-30
		CA-A- 1198699	85-12-31
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